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NATURAL WEATHERING OF SCOTS PINE (*Pinus sylvestris* L.) BOARDS MODIFIED WITH FUNCTIONALISED COMMERCIAL SILICONE EMULSIONS

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A quat-silicone micro-emulsion (particle size <40 nm), an amino-silicone macro-emulsion (110 nm), and an alkyl modified silicone macro-emulsion (740 nm) were used to modify Scots pine (*Pinus sylvestris* L.) sapwood. Treated and uncoated boards were exposed to natural weathering for one year along with water treated controls according to EN 927-3. The treatment with silicone emulsions did not enhance the color stability, which was assessed at three months intervals using a spectrophoto-meter and classified according to the CIE-Lab system. Treatment with amino-silicone emulsions gave a more yellowish appearance of the wood surface before weathering than the other silicones and the control. Boards treated with quat- and amino-silicone were less overgrown by staining fungi and displayed reduced surface roughness than those treated with alkyl-modified silicone and the control samples.

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INTRODUCTION

Solar radiation is an important factor for the deterioration of wood surfaces exposed outdoors. Surface weathering is attributed to the photo-degradation of the wood cell wall components (Gellerstedt and Petterson 1977) by ultraviolet light of solar irradiation that can penetrate up to 75µm into the surface (Kalnins 1966; Hon and Ifju 1978; Hon and Feist 1980a, 1980b). Lignin absorbs most (80-90%) of the UV light, followed by holocellulose (5-20%) and the extractives (Norrström 1969). Photo-degradation of lignin is initiated by rapid oxidation under UV and visible light, which leads to the degradation of the aromatic polymer (Lin and Gierer 1972; Hon 1981a, 1981b). The initial oxidation of lignin results in the formation chromophores due to free radical reactions (Lin et al. 1970). Aromatic sites and other chromophores are further oxidized over time, leading to the formation of carbonyl and carboxyl groups (Hon 1991). All of these newly formed groups change the appearance of the wood surface to a darker color (Dirckx et al. 1992). In the further course of weathering, cleavage products of lignin are washed out by rain water, causing lightening of the surface (Hon 1973; Feist 1982). The lightening is counteracted by colonization of the surface through staining fungi, which cause the typical grey coloration of long-time exposed wood. These fungi are able to metabolize photo-degraded lignin, holocellulose, and derived sugars. The most

important fungal strain within this specific ecological niche are the ascomycetes *Aureobasidium pullulans* and *Sclerophoma pithyophila* (Eaton and Hale 1993; Schoeman and Dickinson 1997). *Hormonema dematioides* is another species responsible for blue staining of wood (Ray et al. 2004).

Photo-degradation of cell wall polymers causes separation and strength loss of wood cells (Hon 2001). Additional leaching of degradation products brings about greater surface roughness (washboard effect) due to the more rapid degradation of less dense earlywood. After leaching of UV degradation products, underlying cell layers are exposed and further eroded (Feist 1982). Surface roughness is increased through checking or cracking due to repeated swelling and shrinking of weathered wood (Chang et al. 1982; Miniutti 1967, 1973; Urban 2005). Measuring the surface texture and its characterization in terms of roughness has been used in several studies to analyze the effects of weathering on wood surfaces (Kamdem and Zhang 2000; Kamdem and Greiler 2002; Xie et al. 2008a).

Photo-degradation and surface roughening, along with fungal colonization, drastically affects the aesthetic appearance of wood and surface protection is therefore of significant economic importance (Anderson et al. 1991). Opaque coatings are conventionally used to protect wood surfaces from weathering. These coatings contain pigments that screen the wood surface from the deleterious effects of solar radiation. The use of clear coatings keeps the wood surface visible, but does not provide protection against solar radiation. Therefore, UV absorbers (UVAs) and radical scavengers such as hindered amine light stabilizers (HALS) or phenolic light stabilizers (N-Oxyl, TEMPO) are added to the coatings in order to restrict the amount of UV radiation that reaches the wood surface (Miller and Boxall 1984; Ahola 1991; de Meijer and Militz 2000).

Chemical wood modification was additionally shown to improve the performance of outside weathered wood. Acetylation with acetic anhydride reduced the crack formation on unfinished wood and/or improved the coating performance due to higher dimensional stability (Beckers et al. 1998; Plackett et al. 1992; Evans et al. 2002). Treatment with methylated 1,3-dimethylol-4, 5-dihydroxyethyleneurea (mDMDHEU) reduced surface discoloration of uncoated panels through staining fungi. Panels treated with mDMDHEU exhibited less deformation (cupping) and crack formation of uncoated and coated panels (Tomazic et al. 2004; Xie et al. 2005, 2006, 2008a).

Silicones (polydimethylsiloxanes) have been reported to impart hydrophobicity, as well as to improve dimensional stability to wood (Weigenand et al. 2007; Ghosh et al. 2008a). In laboratory tests, functionalized silicones bearing primary and secondary amino or quaternary ammonium groups reduced the colonization by blue stain and mould fungi on wood surfaces (Ghosh et al. 2008a) and increased resistance to decay fungi (Weigenand et al. 2008; Ghosh et al. 2008b).

The aim of this study was to evaluate the weathering performance of wood boards treated with commercial silicone emulsions, which were recently tested in the laboratory (Ghosh et al. 2008a, b). After 12 months of natural weathering, the boards were assessed in terms of color change, crack formation and infestation by staining fungi.

EXPERIMENTAL

Chemicals

Quat-silicone micro-emulsion (QuatSiMiE), amino-silicone macro-emulsion (AminoSiMaE), and alkyl-modified silicone macro-emulsion (AlkylSiMaE) with particle size <40 nm, 110 nm and 740 nm respectively were supplied by Momentive GmbH (Leverkusen, Germany). All emulsions contained 35% (wt/wt) silicone (Table 1). In order to adjust the treatment concentration, the stock solutions were diluted with demineralized water, considering the silicone content (Ghosh et al. 2008a).

Table 1. Names and Chemical Properties of the Silicone Emulsions Tested

Formulation	Emulsion particle (nm)	Silicone content (%)	Solid content (%)	N-content (mmol g^{-1})	Structure of functional group
Quat silicone micro-emulsion (QuatSiMiE)	<40	35	47	0.25	Quaternary ammonium, R^1-N^+(CH_3)$_2$-R^{2*}
Amino silicone macro-emulsion (AminoSiMaE)	110	35	38	0.25	Amino, $(CH_2)_3$-NH_2
Alkyl modified silicone macro-emulsion (AlkylSiMaE)	740	35	38.5	0	Alkyl modified, ($-CH_{12}$-C_{14})

[*]The quat−groups are incorporated into the dimethylsiloxane chain (Polymer−CH_2−N^+(CH_3)$_2$−CH_2−Polymer)

Natural Weathering

Scots pine (*Pinus sylvestris* L.) sapwood boards (75 x 15 x 150 mm^3, r x t x l) were impregnated (100 mbar vacuum, 1h; 12 bar pressure, 1h) with 5% and 15% silicone solutions and gradually dried from 30° to 103°C. Water-impregnated and dried boards served as a control. Five samples per treatment were used for the test. The weight percent gain (WPG) of the treated specimens was calculated from the dry masses before and after treatment. The end grains of the specimens were sealed with the coating Wapex 660 (Akzo Nobel Decorative Coatings, Hunsdorf, Germany). The specimens were placed on weathering racks in the test field of the Georg-August University, Göttingen (Germany) for 12 months (August 2007 to August 2008) according to EN 927-3 (2006). Every three months, interval color change and surface roughness were determined after conditioning the specimens at 20°C and 65% RH for one week.

Color Measurement

The color of the specimens was determined with a spectrophotometer CM500, equipped with a standard illuminant D65 (Minolta, Japan) using the CIE-Lab system,

$$\Delta L_t^* = L_t^* - L_i^* \tag{1}$$

$$\Delta a_t^* = a_t^* - a_i^* \tag{2}$$

$$\Delta b_t^* = b_t^* - b_i^* \qquad (3)$$

$$\Delta E_t^* = [(\Delta L_t^*)^2 + (\Delta a_t^*)^2 + (\Delta b_t^*)^2]^{1/2} \qquad (4)$$

$$C = [a_t^2{}^* + b_t^2{}^*]^{1/2} \qquad (5)$$

where, L^* is the lightness (ranging from 0 or black to 100 or white), a^* and b^* are the chromaticity coordinates (+a refers to red, –a refers to green coloration, while +b and –b respectively denote yellow and blue), the subscripts i and t are the initial time and the time after weathering (e.g. t = 3, 6, 9, 12 weeks), ΔL_t^*, Δa_t^* and Δb_t^* are changes of lightness and the color coordinates, ΔE^* is the color change due to weathering, and C is the chroma (color described by the coordinates a and b running from red to green and yellow to blue, respectively).

FT-IR Spectra of Weathered Boards

At the end of the test duration, Fourier-transform infrared (FT-IR) spectra of silicone-treated and untreated, weathered board surfaces were taken using a Vector 22 spectrometer (Bruker, Bremen, Germany) with an ATR unit (DuraSamplIR II, SensIR Technologies, Danbury, USA) operating on 32 scans and at 4cm^{-1} resolution. Background spectra were recorded using an empty ATR unit.

Macroscopic Surface Appearance

In order to assess the effect of weathering on the macroscopic appearance, the board surfaces were scanned before and after weathering using an Epson Expression 10000XL scanner (Epson, UK).

Surface Roughness

The surface texture (average roughness) of the weathered boards was determined using a Perthometer S4P (Feinprüf Perthen GmbH, Göttingen, Germany). The needle had a cone shaped FRW 750 stylus tip with an angle of 60° and a radius of 10 μm. The measuring length was 40 mm vertical to the grain over the tangential surface. The profile filter was a phase-corrected (Gaussian) filter with a cut-off wavelength of 8 mm. Shorter wavelengths than this are considered under the roughness; larger wavelengths under waviness (DIN 4768, 1990). Five specimens were measured for every treatment, and four measurements were taken on each weathered surface. Three modes were used to characterize the average roughness, i.e., R_a represents the average deviation of the roughness profile, but it does not differentiate between the peaks and valleys of a surface profile (Maldas and Kamdem 1998); R_z considers the mean of peak to valley height and R_{max} the maximum roughness depth (Hiziroglu 1996). The relative roughness (R') for all parameters i.e., R_a', R_z' and R'_{max} were calculated using the Eqn. 6,

$$R' = R_t/R_o \qquad (6)$$

where, R_t is the roughness parameter of wood after weathering and R_o is the value of respective specimens before weathering.

Statistical Analysis

The variables considered for the colour change were ΔE, ΔL, Δa, and Δb. As the data were not normally distributed, the results were analyzed by non-parametric one-way ANOVA using the Kruskal-Wallis test. The experimental factor considered was chemical, and the results were grouped by concentration. The comparison between means was performed by the Kruskal-Wallis test with a probability level of 0.05.

RESULTS AND DISCUSSION

Color Measurement

Independent from weathering, the treatment of wood with silicone emulsions changed the color parameters compared to water treatment (controls). Lightness was reduced (Fig. 1A), while the chroma increased (Fig. 1B, see values before weathering, t = 0 month). Changes of lightness and chroma were higher at higher silicone content. This phenomenon can be attributed to functional groups of the silicones. Treatment with amino-silicone (AminoSiMaE) caused the greatest shift in the chroma attributable to higher Δb-value, i.e., a yellowing of the boards.

After weathering, the boards treated with quat- (QuatSiMiE) and amino-silicone emulsions (AminoSiMaE) displayed similar color changes (ΔE) as the controls, while the specimens treated with alkyl-modified silicone (AlkylSiMaE) showed a higher ΔE-value after weathering (Table 2).

Table 2. WPG, ΔE^*, ΔL^*, Δa^* and Δb^* of Scots Pine Specimens after 12 Months of Natural Weathering

Treatment	Con. (%)	WPG (%)	Color components			
			ΔE^*	ΔL^*	Δa^*	Δb^*
QuatSiMiE	5%	8.3±0.9	35.8±3.1(abc)	27.6±4.0(a)	5.0±1.0(abc)	22.1±1.1(a)
AminoSiMaE		6.5±0.9	36.1±2.5(b)	22.4±4.0(b)	5.8±1.7(b)	27.3±2.7(b)
AlkylSiMaE		7.8±0.4	38.6±3.8(c)	31.2±3.9(c)	4.2±1.6(c)	22.1±3.1(a)
Control	-	-	36.2±2.8(abc)	28.1±3.3(ac)	4.4±0.9(ac)	22.3±1.2(a)
QuatSiMiE	15%	16.4±1.9	31.9±1.4(*a*)	22.2±2.0(*a*)	5.5±0.5(*a*)	22.2±1.3(*abc*)
AminoSiMaE		15.3±4.3	37.5±2.0(*b*)	20.7±3.1(*a*)	6.5±1.2(*b*)	30.4±2.0(*b*)
AlkylSiMaE		16.3±1.3	45.7±3.3(*c*)	39.4±3.7(*b*)	3.5±0.8(*c*)	22.5±3.5(*ac*)
Control	-	-	36.2±2.8(*d*)	28.1±3.3(*c*)	4.4±0.9(*d*)	22.3±1.2(*ac*)

(Letter within brackets shows statistical significance of treatments. Same letter indicates no significant difference, when p>0.05)

The color changes (ΔE) of the AlkylSiMaE-treated boards were mainly caused by the change in lightness (ΔL), which is attributable to the colonization of the wood surface by staining fungi (Table 2, also see below). Accordingly, AminoSiMaE-treated boards exhibited the lowest ΔL-value, i.e. the lowest degree of fungal colonization. Recently results from laboratory experiments revealed that AminoSiMaE was the most effective and AlkylSiMaE the least effective formulation in preventing blue stain infestation (Ghosh et al. 2008a). The relatively high ΔE-value of the AminoSiMaE-treated boards is

attributable to the high Δb-value which indicates yellowing of the surfaces and might be caused by oxidation of the amino-groups in the silicone (Xie et al. 2008b).

Maximum reduction in lightness and chroma occurred during the first three months of weathering in treated and control boards (Fig. 1) and diminished afterwards to a more or less similar velocity.
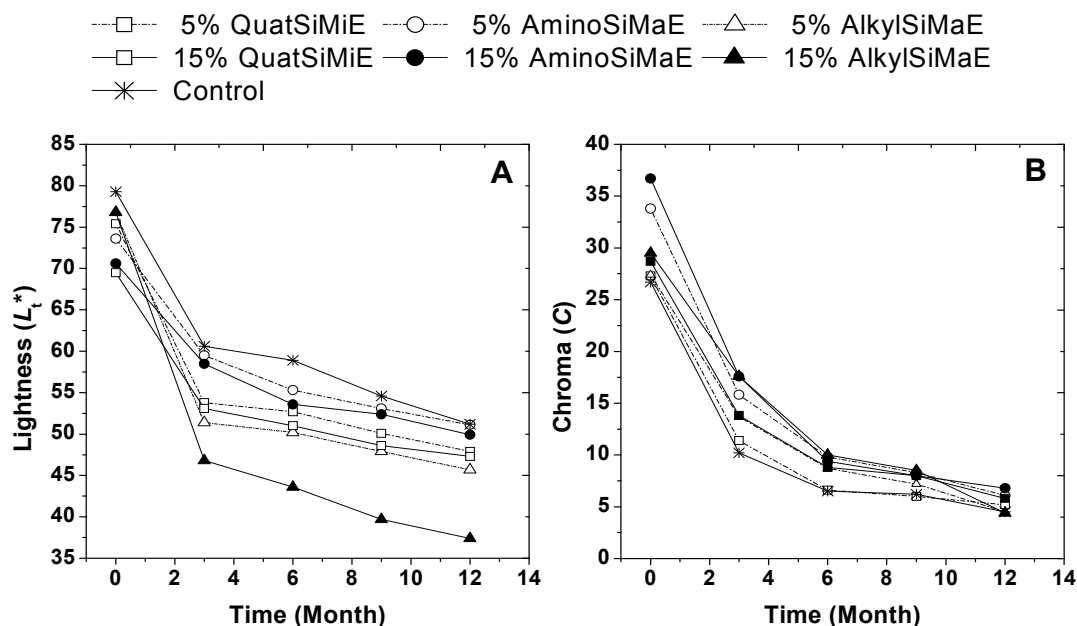

Fig. 1. Change of lightness (L_t^*) and Chroma (C) of silicone-treated and untreated Scots pine boards

This decrease is due to the degradation and wash-out of chromophoric lignin in the initial phase of exposure and due to fungal colonization (Donath et al. 2007). Depolymerization of lignin and other wood components is mainly caused by the UV light of solar irradiation (Hon and Chang 1985) within the region ranging from 300 to 550nm (Leary 1968; Davidson 1996). The reduction of lightness and chroma of silicone-treated Scots pine ensures that the treatment cannot protect lignin from photo-degradation. The finding is in agreement with Ghosh et al. (2008a), reporting the breakdown of lignin in artificially weathered Scots pine treated with the same silicone emulsions.

FT-IR Spectra of Weathered Boards

All unweathered boards displayed absorption peaks at 1505 cm⁻¹, 1600 cm⁻¹ (both aromatic stretch), and 1450 cm⁻¹ (CH$_2$ deformation), which are assigned to lignin (Faix 1992; Faix et al. 1992). Natural weathering caused break down of lignin due to UV light, particularly evidenced from the diminished adsorption band at 1505 cm⁻¹. UV-degradation of lignin was not reduced by the silicone treatment (Fig. 2).

Silicone-treated samples showed absorption bands at 1257 cm⁻¹ assigned to stretch vibration ν(Si-C), 1080 cm⁻¹, and 1000 cm⁻¹ assigned to skeletal vibrations δ(Si-O-Si) and 798 cm⁻¹ assigned for ν(Si-C) and/or ν(Si–O) (Noll 1968; Zollfrank 2001; Zollfrank and Wegener 2002; Sèbe et al. 2004; Tinguat et al. 2005). These bands showed

only minor changes in absorption after weathering (Fig. 2). This indicates that the silicone compounds hardly leached during weathering and were not degraded by UV light. Comparable results were obtained for pine wood boards treated with the same silicone formulations at artificial weathering in a QUV machine (Ghosh et al. 2008a).
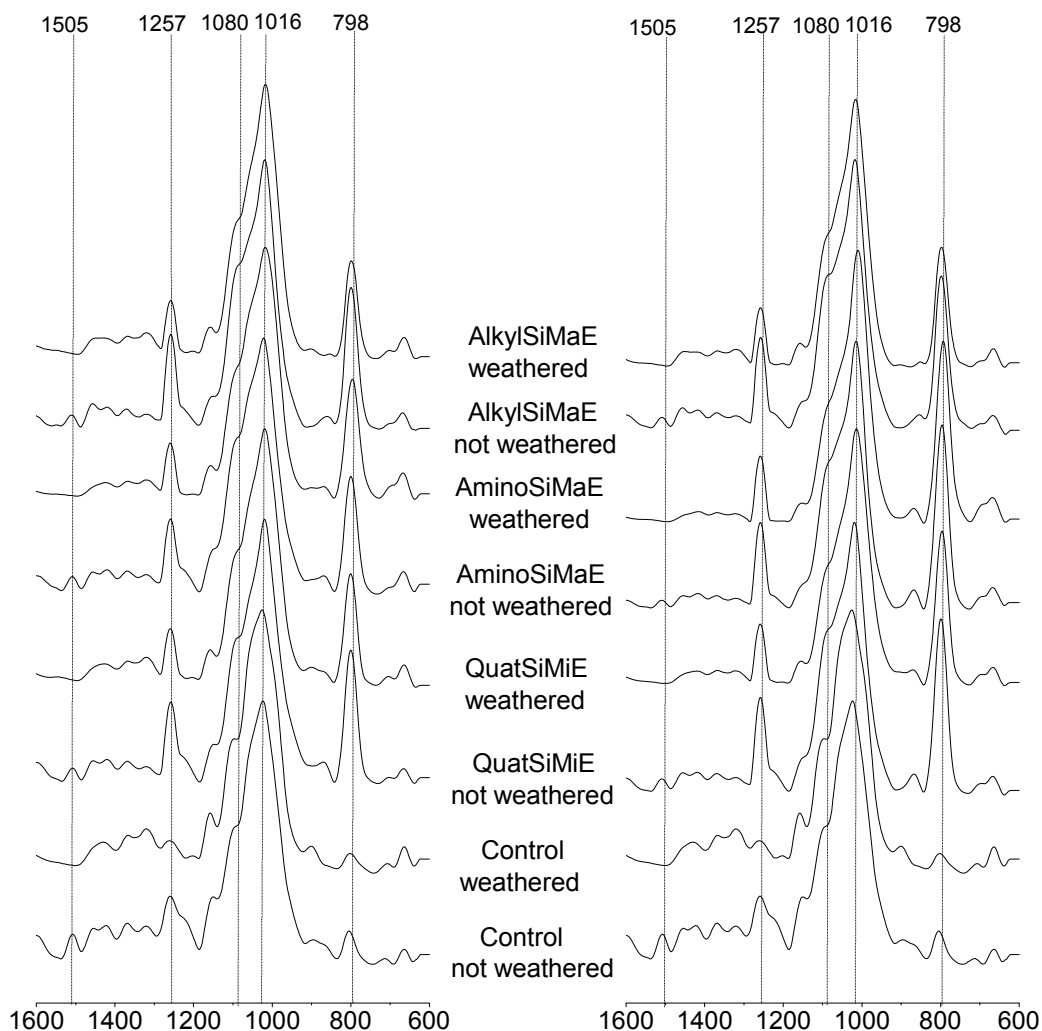

Fig. 2. FT-IR spectra of silicone emulsions treated and untreated Scots pine boards. Spectra in the left column are of 5% silicone and the control, while those in the right column are of 15% silicone and the control.

Macroscopic Surface Appearance

The exposed surfaces of the control specimens and of the boards treated with low and high concentrations of AminoSiMaE displayed a grey staining of similar intensity after weathering (Fig. 3c, g). In contrast, the surfaces of the boards treated with QuatSiMiE appeared to be slightly darker (Figure 3a), while those treated with AlkylSiMaE were clearly darker (Figure 3e) than the control boards.
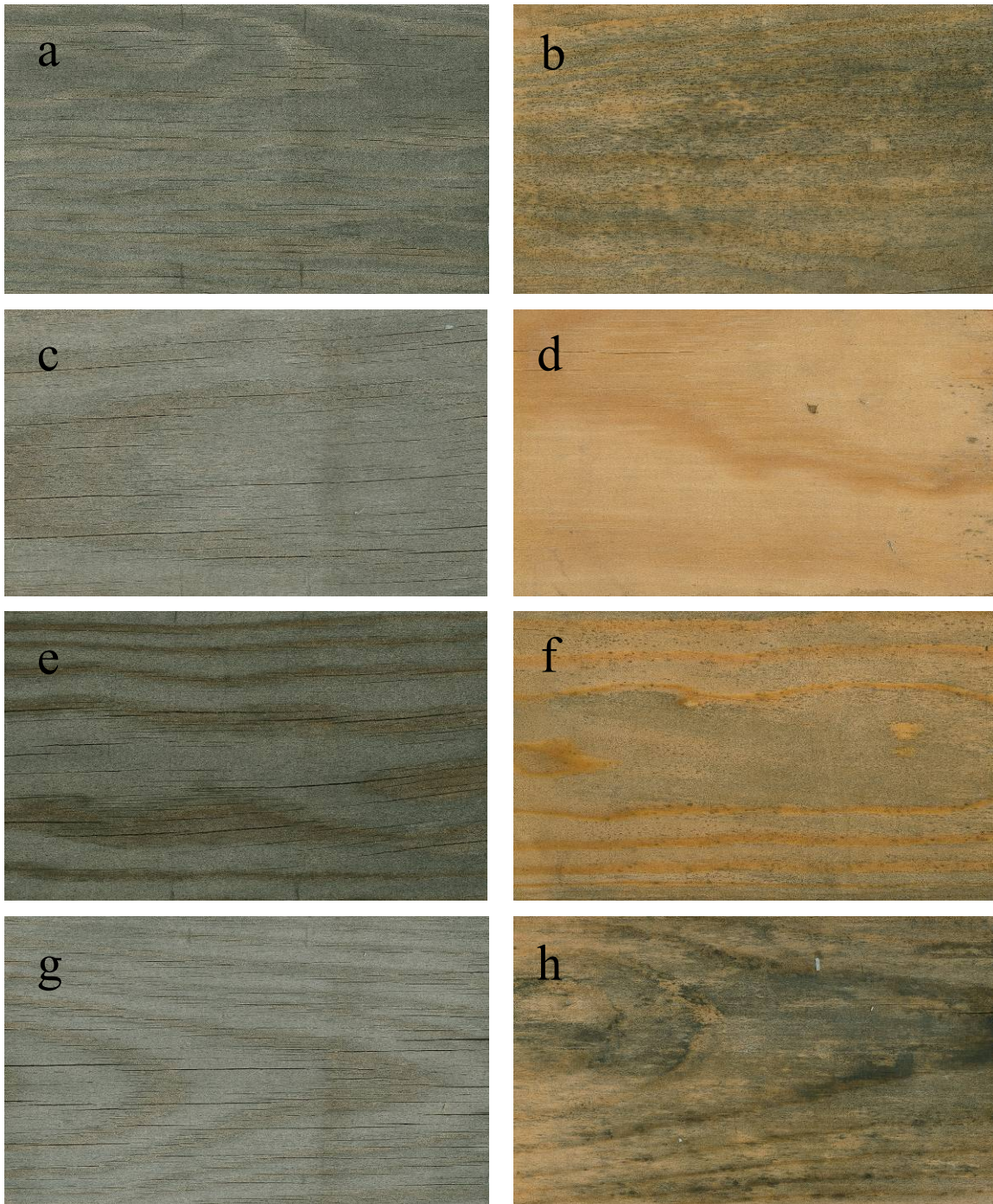
Fig. 3. Appearance of wood surfaces treated with 15% solution of QuatSiMiE, front (a) and reverse (b), AminoSiMaE, front (c) and reverse (d); AlkylSiMaE, front (e) and reverse (f), untreated control, front (g) and reverse (h) after 12 months of natural weathering

The appearance of the reverse, indirectly exposed surfaces gave evidence of the growth of staining fungi. The lowest degree of fungal staining was found in the case of AminoSiMaE-treated specimens at both silicone concentrations, followed by the boards

treated with AlkylSiMaE, QuatSiMiE, and the controls. It was recently shown that AminoSiMaE strongly reduced the growth of staining and mould fungi in laboratory tests. The resistance of QuatSiMiE-treated wood was lower than that treated with AminoSiMaE, while treatment with AlkylSiMaE did not increase the resistance compared to the control (Ghosh et al. 2008a). With regard to the staining of the reverse surface, AlkylSiMaE appeared to be more effective in reducing fungal staining than QuatSiMiE. This might be due to the more hydrophobic nature of the alkyl-modified silicone compared to the quat-silicone (Ghosh et al. 2008a). As a consequence, AlkylSiMaE might prevent the penetration of rain water through the boards more efficiently than QuatSiMiE and, thus, reduces the availability of moisture for the staining fungi on the reverse, indirectly exposed surface.

Greying of weathered wood at direct exposure to sunlight can be divided into three phases. In the first phase, the cell wall polymers are degraded mainly by UV-light. Lignin is the most susceptible compound for UV degradation, although holocellulose has also been shown to undergo severe breakdown (Feist 1990; Hon 1981a; Norrström 1969). In the second phase, these degradation products are washed out by rain water. Under sterile conditions, this process causes whitening of wood due to the predominance of surface cellulose. In the third phase, the degraded surface is colonized by staining fungi, which are able to metabolize photo-degraded lignin, holocellulose and derived sugars (Eaton and Hale 1993; Schoeman and Dickinson 1997). A protective, hydrophobing agent such as a silicone cannot prevent photo-degradation of the cell wall polymers (first phase), but it might be able to reduce leaching of decay-products and fungal colonization (phase 2 and 3). AminoSiMaE and AlkylSiMaE were, however, only able to clearly reduce fungal infestation of the reverse sides of the boards, but not of the front sides. It was shown in laboratory tests that AminoSiMaE and QuatSiMiE effectively prevented the infection of Scots pine sapwood by *A. pullulans and Sclerophoma pithiophyla* (Ghosh et al. 2008a).

The findings in this study seem to indicate that water repellence was the major factor in reducing fungal colonization of the reverse side of the boards. However, water repellence seemed to play a minor role when the surface was directly exposed to weathering. As indicated previously (Ghosh et al. 2008a) as well as in this study, the low fungal resistance of the weathered surface cannot be attributed to washing out of the silicones, which is evident from the FT-IR spectroscopy.

Another reason for the different results of the laboratory tests and natural weathering could be the availability of cell wall degradation products. In the laboratory test performed by Ghosh et al. (2008a) all the degradation products of artificial weathering were removed in a QUV prior to the infestation of the wood surface with a spore suspension of staining fungi. Therefore, the fungi could not feed on the decay products caused by UV light. During natural weathering, however, cell wall degradation products are continuously produced and are available for fungal growth. Therefore, the natural weathering conditions favor fungal growth over the long-term, so that the silicone treatment cannot develop the same effectiveness as under laboratory conditions.

Surface Roughness

The values of the relative roughness parameter R' of weathered specimens indicate that 12 months outdoor exposure resulted in the formation of rough and wavy surfaces (Table 3). According to Kamdem and Grelier (2002) R' value close to 1 indicates little to negligible changes of the wood surface roughness. The treatment of wood with silicone emulsions at low concentration (5%) performed similar to the control samples (Table 3). Treatment with higher concentration (15%), however, resulted in reduced R' values of specimens treated with QuatSiMiE and AminoSiMaE compared to specimens treated with AlkylSiMaE and the controls. The reduced R' values indicated smoother surfaces and fewer cracks, while AlkylSiMaE-treated and control specimens displayed more and wider cracks on the exposed surface.

Table 3. Relative Surface Roughness Parameters of Silicone-Treated and Untreated Scots Pine Boards

Treatment	Con. (%)	WPG (%)	R'_a (µm)	R'_z (µm)	R'_{max} (µm)
QuatSiMiE		8.3±0.9	3.3±0.7(a)	3.6±0.8(a)	3.3±1.1(a)
AminoSiMaE	5%	6.5±0.9	3.4±0.7(a)	3.7±1.1(a)	3.4±0.4(b)
AlkylSiMaE		7.8±0.4	3.5±1.0(a)	3.8±1.8(a)	3.5±0.9(bc)
Control	-	-	3.8±0.9(a)	3.9±1.1(a)	3.8±1.7(d)
QuatSiMiE		16.4±1.9	2.1±0.5(*a*)	1.9±0.6(*a*)	2.1±0.6(*a*)
AminoSiMaE	15%	15.3±4.3	2.5±0.8(*b*)	2.4±0.5(*b*)	2.5±1.0(*a*)
AlkylSiMaE		16.3±1.3	3.3±0.6(*bc*)	3.1±0.7(*c*)	3.3±0.6(*b*)
Control	-	-	3.8±0.9(*d*)	3.9±1.1(*d*)	3.8±1.7(*c*)

(Letter within brackets shows statistical significance of treatments. Same letter indicates no significant difference, when p>0.05)

The formation of cracks is attributed to dimensional changes of wood responding to varying moisture conditions. The roughness values of untreated and silicone-treated specimens indicate that roughness increased with increasing exposure time (Fig. 4). Boards treated with low silicone concentration roughened at the same velocity as the untreated specimens. A similar trend was observed for samples treated with 15% concentration of AlkylSiMaE. Surface roughness of QuatSiMiE- and AminoSiMaE-treated boards (at 15% concentration), however, increased more slowly than that of the untreated specimens.

Earlier studies reported that the particle size of silicone emulsions influenced the dimensional stability of Scots pine sapwood. The micro-emulsion of an amino-silicone bearing low particle size caused higher cell wall bulking and anti-swelling efficiency (ASE) than the respective macro-emulsion (Weigenand et al. 2007). Accordingly, QuatSiMiE and AminoSiMaE having clearly smaller particle sizes imparted higher dimensional stability than AlkylSiMaE (Ghosh et al. 2008a). The reduced roughness of the boards treated with QuatSiMiE and AminoSiMaE (15%) can be attributed to the higher dimensional stability of these specimens compared to those treated with AlkylSiMaE. Roughness of the boards treated at low concentration (5%) was similar to that of the controls, because the low silicone concentration brought about minor

dimensional stabilization. QuatSiMiE was shown to cause higher ASE than AlkylSiMaE, while the latter induce higher hydrophobicity than the former (Ghosh et al. 2008a). This seems to indicate that dimensional stabilization was more crucial in terms of cracking reduction than hydrophobation.
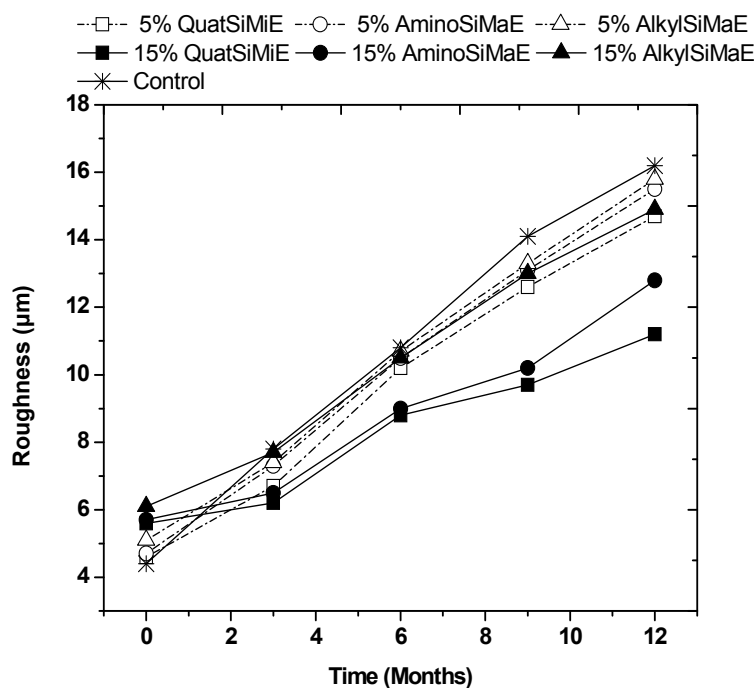

Fig. 4. Roughness of silicone-treated and untreated Scots pine boards measured during 12 months of natural weathering

CONCLUSIONS

1. The silicone emulsions used in this study were not able to reduce the discoloration of surfaces directly exposed to natural weathering. While the boards treated with AminoSiMaE displayed comparable greying, relative to the controls, those treated with QuatSiMiE and AlkylSiMaE turned even darker. These results show, on the one hand, that the used silicones cannot protect the lignin from photo-degradation. On the other hand, the efficacy of silicones against fungal staining under long-term natural weathering conditions is much lower than that observed in laboratory tests (Ghosh et al. 2008a).

2. In contrast, all silicones reduced the staining of the reverse, indirectly weathered sides of the boards. This effect can be attributed to hydrophobation of the entire board, which inhibits the migration of moisture from the front to the reverse surface.

3. The QuatSiMiE and AminoSiMaE reduced surface cracking to a higher degree than AlkylSiMaE. The effect is mainly attributed to a higher dimensional stabilization imparted by the amino- and quat-silicone rather than to hydrophobation.

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